EUROPHYSICS LETTERS 1 February 2001

Europhys. Lett., **53** (3), pp. 354–359 (2001)

A new heavy-fermion superconductor $CeIrIn_5$: A relative of the cuprates?

C. Petrovic[1,2], R. Movshovich[1], M. Jaime[1], P. G. Pagliuso[1], M. F. Hundley[1], J. L. Sarrao[1], Z. Fisk[1,2] and J. D. Thompson[1](*)

[1] *Condensed Matter and Thermal Physics, Los Alamos National Laboratory Los Alamos, NM 87545 USA*

[2] *National High Magnetic Field Laboratory, Florida State University Tallahassee, FL 32306 USA*

(received 18 July 2000; accepted in final form 22 November 2000)

PACS. 71.27.+a – Strongly correlated electron systems; heavy fermions.
PACS. 74.70.Tx – Heavy-fermion superconductors.

Abstract. – $CeIrIn_5$ is a member of a new family of heavy-fermion compounds and has a Sommerfeld specific-heat coefficient of $720\,\mathrm{mJ/mol\,K^2}$. It exhibits a bulk, thermodynamic transition to a superconducting state at $T_c = 0.40\,\mathrm{K}$, below which the specific heat decreases as T^2 to a small residual T-linear value. Surprisingly, the electrical resistivity drops below instrumental resolution at a much higher temperature $T_0 = 1.2\,\mathrm{K}$. These behaviors are highly reproducible and field-dependent studies indicate that T_0 and T_c arise from the same underlying electronic structure. The layered crystal structure of $CeIrIn_5$ suggests a possible analogy to the cuprates in which spin/charge pair correlations develop well above T_c.

Of the vast number of metallic compounds, only a small fraction enters a superconducting state at low temperatures, and of this small number, an even smaller fraction develops superconductivity out of a normal state in which electronic correlations produce orders-of-magnitude enhancement of the conduction electrons' effective mass [1]. This subset of materials, known as heavy-fermion superconductors, has been an influential area of research in condensed-matter physics since its first member $CeCu_2Si_2$ was discovered [2] in 1979. Unlike all previously known superconductors, the presence of a magnetic ion (in this case Ce) was essential for superconductivity and the temperature dependence of physical properties below the superconducting transition temperature T_c was inconsistent with the well-established Bardeen-Cooper-Schrieffer theory of superconductivity. Over the past two decades other examples have been added to this class: five uranium-based compounds at atmospheric pressure and five cerium-based systems in which heavy-fermion superconductivity has been induced by applying pressure [3]. Interestingly, all but two of the pressure-induced heavy-fermion superconductors and one U-based superconductor form in the same $ThCr_2Si_2$ tetragonal structure as $CeCu_2Si_2$, suggesting that this structure type is particularly favorable for heavy-fermion superconductivity. The two notable Ce-based exceptions have a common denominator as well, $CeIn_3$. Cubic $CeIn_3$, when subjected to 25 kbar pressure, becomes a superconductor below

(*) E-mail: jdt@mst.lanl.gov

about 0.15 K [4], and $CeRhIn_5$, composed of layers of $CeIn_3$, superconducts below 2.1 K for pressures above 17 kbar [5]. These two recent discoveries suggest that heavy-fermion superconductivity might be found in structurally related materials.

Experimental and theoretical study of the superconductivity in these heavy-fermion materials has formed a substantial basis for understanding more broadly classes of unconventional superconductors, including the high-T_c cuprates, in which the electron-pairing interaction responsible for superconductivity may be mediated by spin fluctuations [1]. In spite of progress, the heavy-fermion problem and heavy-fermion superconductivity in particular remain challenges to experiment and theory [6]. Though heavy-fermion behavior has been found in several structure types, it appears that, like conventional BCS superconductivity, heavy-fermion superconductivity may be favored by particular crystallographic structures. Because of the limited number of examples, we know very little about relationships that should exist between the structure and properties of these materials. Any predictive understanding of how superconductivity can emerge in the highly correlated ground state has to be able to explain why it appears in one crystal structure and not another. This makes the discovery of a new prototype structure for heavy-fermion superconductivity of special interest. Here, we report a new ambient-pressure Ce-based heavy-fermion superconductor that is isostructural to $CeRhIn_5$, suggesting that this structure, like the $ThCr_2Si_2$ structure, may be particularly favorable for superconductivity. Unlike $CeCu_2Si_2$, this new compound grows easily and reproducibly as large, very pure single crystals, opening the possibility for unprecedented study.

$CeIrIn_5$ is a member of this new family that forms as $R_nT_mIn_{3n+2m}$, where $n = 1$ or 2, $m = 1$, R = La through Gd (except Eu), and T is a transition metal. All members grow readily as cm-sized, plate-like single crystals out of an In-rich flux. Crystals were obtained by combining stoichiometric amounts of Ce and T with excess In in an alumina crucible, encapsulating the crucible in an evacuated quartz ampoule, heating to 1100 °C, and slowing cooling to 600 °C. At this temperature, the ampoule was removed from the oven and the excess In removed by centrifugation. Powder X-ray patterns obtained on crushed single crystals show that $CeIrIn_5$ crystallizes in the tetragonal $HoCoGa_5$ structure type, with $a = 4.668(1)$ Å and $c = 7.515(2)$ Å [7]. Within typical resolutions of X-ray diffraction, microprobe analysis, and differential scanning calorimetry, the $CeIrIn_5$ crystals are single-phase. Compounds for which $n = 1$ can be viewed as alternating layers of $CeIn_3$ and TIn_2 stacked sequentially along the tetragonal c-axis and for $n = 2$ form as bilayers of $CeIn_3$ separated by a single layer of TIn_2. A large resistivity ratio $\rho(300\,\mathrm{K})/\rho(2\,\mathrm{K}) = 50$–80 for the Ce materials attests, in part, to the high quality of the crystals as does the observation of resolution-limited Laue diffraction and NQR spectra. The hallmark of a heavy-fermion system is the magnitude of its electronic coefficient of specific heat γ, which is a measure of the effective mass enhancement of conduction electrons produced by electronic correlations [1]. All of the Ce-based members of this new family exhibit heavy-fermion behavior as indicated by their large Sommerfeld specific-heat coefficients γ, which range from $\approx 400\,\mathrm{mJ/mole\ Ce\ K^2}$ for antiferromagnetic $CeRhIn_5$ and Ce_2RhIn_8 to $\approx 700\,\mathrm{mJ/mole\ Ce\ K^2}$ for $CeIrIn_5$ and Ce_2IrIn_8. In contrast, the La analogues, which do not contain an f-electron, are Pauli paramagnets with coefficients γ of about $5\,\mathrm{mJ/mole\ K^2}$ that are typical of simple metals. Additional details of the preparation and characterization of this family will be given elsewhere.

The overall temperature dependence of the resistivity ρ and magnetic susceptibility χ of $CeIrIn_5$ is shown in fig. 1. The magnetic susceptibility is anisotropic, with χ larger by nearly a factor of two at low temperatures for a magnetic field applied along the tetragonal c-axis. Plots of $1/\chi$ are linear in temperature for $T \geq 200\,\mathrm{K}$. From the linear regime, we find a paramagnetic Curie temperature Θ_P, which is $+12.5\,\mathrm{K}$ ($-67.4\,\mathrm{K}$) for a magnetic field of 1 kOe applied parallel (perpendicular) to the c-axis. A polycrystalline average of the

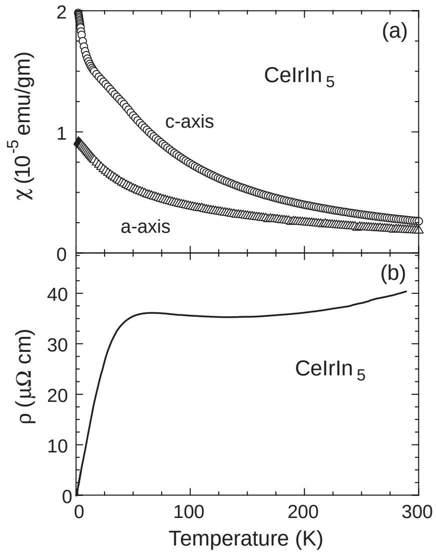

Fig. 1 – (a) Magnetic susceptibility χ as a function of temperature for a 1 kOe field applied parallel to the c- (circles) and a-axis (triangles) of $CeIrIn_5$. Measurements were made in a Quantum Design Superconducting Quantum Interference Device magnetometer. (b) Electrical resistivity ρ *vs.* temperature measured with a 4-lead ac resistance bridge.

high-temperature data gives an effective moment $\mu_{\mathrm{eff}} = 2.28\mu_{\mathrm{B}}$ that is reduced somewhat from the free-ion moment of Ce^{3+}, $2.54\mu_{\mathrm{B}}$, due to the presence of crystalline electric fields that lift the degeneracy of the $J = 5/2$ Hund's rules multiplet. Characteristic of Ce-based heavy-fermion compounds, the resistivity passes through a maximum at low temperatures that typically is attributed to the cross-over from strong, incoherent scattering of electrons at high temperatures to the development of strongly correlated bands at low temperatures. The magnitude and temperature dependence of ρ are similar to those of the heavy-fermion antiferromagnet $CeIn_3$ [4].

Thermodynamic and transport properties of $CeIrIn_5$ at low temperatures are summarized in fig. 2. Above 0.4 K, the specific heat divided by temperature $C/T \equiv \gamma = 720\,\mathrm{mJ/mole\,K^2}$ and is nearly temperature independent. At $T_{\mathrm{c}} = 0.40\,\mathrm{K}$, there is a jump in C/T and a prominent signature in ac susceptibility χ_{ac}. Comparing the magnitude of this χ_{ac} response to that of a piece of superconducting tin having a similar size and shape as the $CeIrIn_5$ sample, we estimate that the χ_{ac} signature corresponds to a change in susceptibility of $-(1 \pm 0.1)/4\pi$, as expected for a bulk superconductor. From the average of measurements on three different crystals, the specific-heat jump ΔC at T_{c} is equal to $(0.76 \pm 0.05)\gamma T_{\mathrm{c}}$. This ratio $\Delta C(T_{\mathrm{c}})/\gamma T_{\mathrm{c}}$ is comparable to that found in other heavy-fermion superconductors, such as $CeCu_2Si_2$ and UPt_3 [6], and provides compelling evidence that superconductivity in $CeIrIn_5$ develops among the heavy quasiparticles. The specific-heat data below T_{c} fit well to the sums of nuclear Schottky, T^2 and T-linear contributions. (A nuclear Schottky term is expected due to the large nuclear quadrupole moments of Ir and In [8].) The $C \propto T^2$ contribution suggests that the superconducting gap function goes to zero along certain portions of the Fermi surface [9]. The temperature dependence of the thermal conductivity, which is insensitive to the nuclear Schottky, also is described well from T_{c} to 50 mK by the sum of linear and quadratic terms that are consistent with corresponding terms in the specific heat.

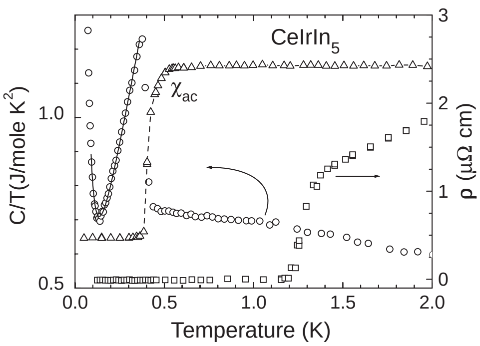

Fig. 2

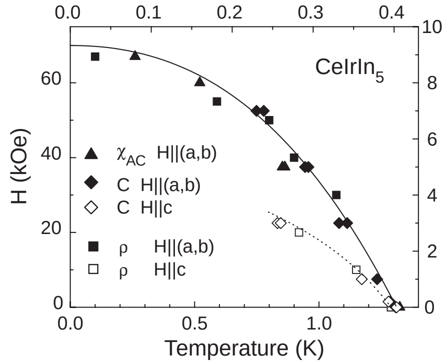

Fig. 3

Fig. 2 – Specific heat divided by temperature C/T (circles, left ordinate), ac magnetic susceptibility χ_{ac} (triangles, arbitrary units) and electrical resistivity ρ (squares, right ordinate) of $\mathrm{CeIrIn_5}$ as functions of temperature. The solid line is a fit to C/T data below half of T_{c} and is given by $C/T\,(\mathrm{J/mole\,K^2}) = 3.9(\pm 0.1)\cdot 10^{-4}/T^3 + 3.5(\pm 0.1)T + 0.03(\pm 0.2)$. The dashed line through $\chi_{\mathrm{ac}}\,(T)$ is a guide to the eye.

Fig. 3 – Magnetic field H *vs.* temperature phase diagram constructed from specific heat C, ac magnetic susceptibility χ_{ac} and electrical resistivity ρ measurements on a $\mathrm{CeIrIn_5}$ crystal with a magnetic field applied parallel and perpendicular to the c-axis. Transition midpoints are used to define the diagram. The left ordinate and bottom abscissa correspond to resistivity data. The right ordinate and top abscissa correspond to specific heat and χ_{ac} data. Open symbols are for H parallel to the c-axis. Solid symbols are for H perpendicular to the c-axis. Note the difference in field and temperature scales and that the anisotropy in these data is identical irrespective of the measurement technique. Solid and dashed lines are guides to the eye.

A peculiar aspect of the data in fig. 2 is that the resistivity drops to zero, or at least to less than our instrumental resolution of $0.01\,\mu\Omega$ cm, at $T_0 = 1.2\,\mathrm{K}$ without a prominent thermodynamic or magnetic signature [10]. As shown in fig. 3, measurements of the specific heat, ac susceptibility and electrical resistivity in magnetic fields applied parallel and perpendicular to the c-axis of $\mathrm{CeIrIn_5}$ find that the anisotropic responses of T_{c}, determined by specific heat and ac susceptibility, and T_0, determined resistively, are identical. Within the scatter of data in fig. 3, these results are reproduced in three independently grown crystals. It is extremely improbable that a secondary phase embedded in each of these crystals would exhibit precisely the same anisotropy as the bulk phase below T_{c}, and, therefore, seems reasonable to conclude that both transitions at T_0 and T_{c} are intrinsic and arise from a common underlying electronic structure that band structure calculations [11] and preliminary de Haas-van Alphen measurements [12] show to be quasi-2D. Though coming from a common electronic background, T_{c} and T_0 develop out of apparently dissimilar manifestations of the highly correlated normal state. Just above T_{c}, the large, nearly constant C/T is typical of a strongly correlated Landau Fermi liquid. However, in all crystals we have studied, the electrical resistivity varies as $\rho(T) - \rho(T_0) \propto T^n$, with $n = 1.3 \pm 0.05$, for $T_0 \le T \le 5\,\mathrm{K}$. This is not the quadratic temperature dependence expected of a Landau Fermi liquid, and it persists unchanged from $\sim 5\,\mathrm{K}$ to 60 mK when a magnetic field is applied to suppress T_0. Similar power law variations in the electrical resistivity are found in the cuprates [13] and in heavy-fermion systems tuned by pressure to a magnetic/superconducting boundary [14]. One suggestion for its origin is the scattering of conduction electrons by antiferromagnetic spin fluctuations whose characteristic wave vector connects portions of the Fermi surface [15]. In this scenario, the lack of a detectable change in the power law indicates that a modest field does not substantially alter the nature of antiferromagnetic fluctuations or Fermi-surface topology of $CeIrIn_5$.

Tuning the hybridization between the $4f$ and ligand electrons by substituting Rh for Ir induces small-moment, incommensurate antiferromagnetism [16] in the end member $CeRhIn_5$, which has a Néel temperature of 3.8 K. Magnetization and nuclear quadrupole-resonance studies indicate similarities [5, 16] of the magnetism in $CeRhIn_5$ with that found in La_2CuO_4 from which high-T_c superconductivity develops with hole doping. When Rh is added substitutionally into $CeIrIn_5$, T_0 decreases and T_c increases, which it also does when $CeIrIn_5$ is subjected to hydrostatic pressure. For $x = 0.25$ and 0.5 in $CeIr_{1-x}Rh_xIn_5$, a small, less than $0.01(-1/4\pi)$, diamagnetic response appears in χ_{ac} at T_0 that is followed by a much larger diamagnetic signal at T_c. Midway between the end-points, $CeIr_{0.5}Rh_{0.5}In_5$, T_c more than doubles to 0.86 K, $\Delta C(T_c)/\gamma T_c$, γ, and $C(T)$ below T_c are virtually unchanged relative to $CeIrIn_5$, and T_0 decreases to 1.0 K. Higher Rh concentrations ($x \geq 0.6$) induce a well-defined magnetic transition in both specific-heat and magnetic susceptibility. These trends with isoelectronic substitution, which tunes f-d hybridization, are similar to those observed in the cuprates [17] with hole doping, which tunes band filling.

The apparently zero-resistivity state below T_0 suggests the presence of a percolating path of superconductivity along the sample. Though possible, it seems unlikely, given the high quality of the crystals and the reproducibility of the effect, that the transition at T_0 arises from chemical or residual stress inhomogeneities in the sample. A possible alternative interpretation comes from an analogy with the cuprates. As a function of temperature and doping in the cuprates, a decrease in, for example, spin susceptibility and electrical resistivity defines a boundary in the T-x phase diagram that marks a cross-over from a paramagnetic to a pseudo-gap state out of which bulk superconductivity develops [18]. Many experiments are consistent with the formation of local (static or dynamic) spin/charge pair correlations without global phase coherence, concepts for which there is growing theoretical support [17]. In the cuprates, this boundary is smeared by inhomogeneity introduced by hole doping. Without such inhomogeneity, one might expect this boundary to become a sharply defined phase transition [19] with signatures similar to those found in our case at T_0. We, however, would expect a specific-heat feature at T_0, but one is not prominent. Quite plausibly this feature is small compared to the large, heavy-electron specific heat out of which it develops and not readily detected within our experimental resolution [10]. Again drawing on the cuprates, the bulk transition at T_c might be interpreted as the (Bose) condensation of electron pairs "preformed" at T_0 or as the temperature at which Josephson coupling among pairs produces global phase coherence throughout the sample.

In summary, the new superconductor $CeIrIn_5$ suggests that the physics of heavy-fermion materials is much richer than previously imagined and that, when crystallizing in a quasi-2D structure, may show features analogous to those in the cuprate superconductors [20]. The search for yet other examples of 2D structure types that form with Ce appears to be a fruitful path of investigation as does additional study of $CeIrIn_5$, which may bridge our understanding of more nearly 3D heavy-fermion metals and the copper oxides.

* * *

Work at Los Alamos was performed under the auspices of the U. S. Department of Energy. ZF acknowledges support through NSF grants DMR-9870034 and DMR-9971348.

REFERENCES

[1] FISK Z. *et al.*, *Science*, **239** (1988) 33.
[2] STEGLICH F. *et al.*, *Phys. Rev. Lett.*, **43** (1979) 1892.
[3] Uranium-based superconductors include UPt_3, $UBe1_3$, URu_2Si_2, UPd_2Al_3 and UNi_2Al_3. Under applied pressure, heavy-fermion antiferromagnets $CeCu_2Ge_2$, $CePd_2Si_2$, $CeRh_2Si_2$, $CeIn_3$ and $CeRhIn_5$ become superconductors.
[4] WALKER I. R., GROSCHE F. M., FREYE D. M. and LONZARICH G. G., *Physica B*, **282-287** (1997) 303.
[5] HEGGER H. *et al.*, *Phys. Rev. Lett.*, **84** (2000) 4986.
[6] GREWE N. and STEGLICH F., in *Handbook on the Chemistry and Physics of Rare Earths*, edited by K. A. GSCHNEIDNER and L. EYRING, Vol. **14** (North Holland, Amsterdam) 1991, p. 343.
[7] The structure type and structural parameters have been confirmed by single-crystal neutron and electron diffraction. MOSHOPOULOU E. G. *et al.*, to be published in *J. Solid State Chem.*
[8] BLEANEY B. and HILL R. W., *Proc. Phys. Soc.* (*London*), **78** (1961) 313.
[9] For a BCS superconductor in which a superconducting gap Δ develops over the entire Fermi surface, $C \propto \exp[-\Delta/k_{\mathrm{B}}T]$. Assuming the simplest model of a spherical Fermi surface, $C \propto T^2$ implies a line of zeros in the gap function.
[10] Inspection of C/T data in fig. 2 suggests a possible a change in slope near 1.2 K that might be expected on the basis of high-sensitivity zero-field ac susceptibility measurements (Gegenwart, private communication) which show a very weak diamagnetic response ($\sim 2 \cdot 10^{-5}(-1/4\pi)$) below 1.2 K.
[11] WILLS J., unpublished.
[12] CORNELIUS A. *et al.*, to be published in *Phys. Rev. B*; GOODRICH R. *et al.*, unpublished.
[13] For example, TAKAGI H. *et al.*, *Phys. Rev. Lett.*, **69** (1992) 2975.
[14] MATHUR N. D. *et al.*, *Nature*, **394** (1998) 39.
[15] MILLIS A. J., MONIEN H. and PINES D., *Phys. Rev. B*, **42** (1993) 167.
[16] CURRO N. J. *et al.*, *Phys. Rev. B*, **62** (2000) R6100.
[17] ORENSTEIN J. and MILLIS A. J., *Science*, **288** (2000) 468.
[18] TIMUSK T. and STATT B., *Rep. Prog. Phys.*, **62** (1999) 61.
[19] See, for example, CHAKRAVARTY S., LAUGHLIN R. B., MORR, D. K. and NAYAK C., cond-mat/0005443 v2.
[20] MONTHOUX P. and LONZARICH G. G., *Phys. Rev. B*, **59** (1999) 14598.